InP is promising material for high-speed transistors, optoelectronic devices and water splitting photoelectrodes due to its high charge carrier mobility. Recently, the formation of porous InP by anodic oxidation in HCl has been demonstrated [1, 2] in analogy to the preparation of porous silicon. This work focuses on the cathodic decomposition and the changes in surface morphology of n-InP (100) plane (S-doped, $N_{\text{d}} = 3.7 \times 10^{10}$ cm$^{-2}$) deaerated 1 M HCl in relation to the formation of porous layer.

Mott-schottky analysis of potential dependent electrochemical impedance spectroscopy (100 mHz ≤ f ≤ 1 MHz) has revealed [3] that the flat band potential is -0.3 V(SHE) for n-InP. If n-InP is cathodically polarized (in dark) in HCl, it decomposes according to

$$\text{In} + 3 \text{H}^+ + 3 e^- = \text{InH}_3$$

in parallel to the hydrogen evolution,

$$2 \text{H}_2 \rightarrow 4 e^- + 2 \text{H}_2$$

The reaction fraction of the cathodic decomposition, $x$, can be coulometrically evaluated if the metallic indium formed on the InP surface during cathodic decomposition is subjected to the following anodic dissolution in the subsequent anodic potential sweep.

$$\text{In} + 4 \text{H}^+ + 3 e^- = \text{In}^2+ + 3 \text{H}_2$$

The lower part of Fig.1 shows the potentiodynamic anodic polarization curves (potential sweep rate : 10 mV s$^{-1}$) of n-InP after cathodic polarization at $E_c = -0.8$ V(SHE) for $t_c$. The anodic current peak at -0.45 V increases with increasing $t_c$, which is ascribed to anodic dissolution of the metallic indium on the InP surface. As shown in the upper part of Fig. 1, the total cathodic charge, $q_c$, required for the reactions (1) and (2) is the sum of $q_{c1}$, at $E_c$ and $q_{c2}$ in the subsequent anodic potential sweep. On the other hand, the anodic charge, $q_a$, of the current peak at -0.45 V is that required for the reaction (3). The following relation, therefore, holds between the ratio, $q_a / q_c$, and the reaction fraction of the cathodic decomposition, $x$.

$$q_a / q_c = 3 x / (x + 2)$$

Fig.2 shows the $q_a / q_c$ and $x$ vs. $t_c$ curves at various $E_c$. It is seen from Fig. 2 that $x$ depends on $t_c$ and $E_c$, and takes a maximum of $x = 0.5$ at $t_c = 50$ s and $E_c = -0.75$ V.

The surface morphology of InP subjected to cathodic polarization at $E_c$ for $t_c$ was observed with an atomic force microscope (AFM). The AFM observation indicated that small particles (0.05 µm - 0.5 µm) of metallic indium with a rectangular shape were deposited on the InP surface due to cathodic decomposition. The size of the indium particles tend to reduce with increasing $t_c$. Moreover, AFM observation was performed for the InP surfaces after anodic stripping of metallic indium particles. The surface roughness of InP increased with increase in the cycle of cathodic decomposition and anodic stripping. The change in surface morphology due to the cyclic decomposition and stripping will be discussed in detail.

References